Electronic Supplementary Information

A sulfurization-based oligomeric sodium salt as a high-performance organic anode for sodium ion batteries

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Experimental details

Materials synthesis

Na₂S·9H₂O, 2,5-dichloro-3,6-dihydroxy-p-quinone (CLA) (Aladdin, 98%), 1-methyl-2-pyrrolidinone (NMP) (Aladdin) were used without further purification. The sodium salt of poly(2,5-dihydroxy-p-benzoquinonyl sulfide) (Na₂PDS) was prepared by the Phillips method and subsequent purification through a simple salification reaction. CLA (0.01 mol), Na₂S·9H₂O (0.02 mol), and NMP (40 ml) were mixed and then kept under magnetic stirring at 150 ºC for 6 h. After cooling to a surrounding temperature, the final product was centrifuged, washed with deionized water, and dried at 70 ºC. In order to further purify the product, the resulting Na₂PDS (0.4 g) was dissolved in 40 ml HCl solution (5 M) under stirring for 36 h. The generated precipitate was then centrifuged, washed with deionized water for several times, and dried at 70 ºC. The intermediate product (0.2 g) of poly(2,5-dihydroxy-p-benzoquinonyl sulfide) (PDS) was also dissolved in 20 ml NaOH solution (5 M) under stirring for 36 h. The obtained dark suspension was then centrifuged to get a dark precipitate of Na₂PDS. It was washed with deionized water for several times and dried at 70 ºC, and a purified product of Na₂PDS was obtained.
Characterization

The morphologies of the products were observed by scanning electron microscopy (SEM, FEI, Sirion 200) and the phase was characterized by X-ray diffraction (XRD) using a X’Pert PRO (PANalytical B.V., 5 Holland) diffractometer. Fourier transform infrared spectra were carried out on a VERTE 70 (Bruker Company, Germany) in the wavenumber range from 400 to 4000 cm\(^{-1}\) at room temperature.

Electrochemical measurement

The Na\(_2\)PDS electrodes were prepared by grinding 60 wt% active material, 30 wt% super P, and 10 wt% PVDF in NMP. Then the slurry was coated onto a clean Cu foil, dried in an oven at 70 °C for 24 h, and cut into wafers with a diameter of 8 mm. The loading of the active material is about 1 mg cm\(^{-2}\). The assembled CR2032 half coin cell consists of the Na\(_2\)PDS electrode, glass fiber membrane (GF/D, Whatman), 1 M NaClO\(_4\) dissolved in a mixture of EC (ethylene carbonate) and PC (polypropylene carbonate) (1:1 by volume) as the electrolyte, and sodium metal as the counter electrode. Galvanostatic charge–discharge tests were tested on a Land Battery Measurement System (Land) and the CV measurements were carried out on an electrochemical workstation (CHI 660D, China). For ex-situ FTIR characterizations, the half cells at different charge and discharge states were disassembled carefully in an Ar-filled glove box with water/oxygen content lower than 1 ppm. Then the relevant electrode slices were rinsed with pure propylene carbonate (PC) solvent for several times and dried in the Ar-filled glove box for several days. The dried and sealed samples with argon gas were taken out and mixed with KBr (in a mass ratio of 1:200) and pressed into tablets for FTIR characterizations.
Fig. S1 The reaction between CLA and Na₂S to prepare Na₂PDS.

Fig. S2 The salification reaction to purify the Na₂PDS product.
Fig. S3 SEM images for the Na$_2$PDS product.

Fig. S4 XRD pattern for the Na$_2$PDS product.
**Fig. S5** Photograph for the solubility of the Na$_2$PDS electrode slices in EC/PC at different charge and discharge stages.

**Fig. S6** Cycling profiles of the Na$_2$PDS electrode at a current density of 100 mA g$^{-1}$. 